THE EFFECT OF LOW-CARBON FUEL ON TRACE METALS, ORGANIC COMPOUNDS, GASEOUS AND PARTICULATE SPECIES FROM A EURO IV DIESEL ENGINE AT STEADY-STATE MODE

ABDULFATAH ABDU YUSUF & Professor FREDDIE L. INAMBAO

Department of Mechanical Engineering, University of KwaZulu-Natal, Durban 4041, Republic of South Africa

ABSTRACT

Diesel engines are a source of heavy pollutants which are of particular concern. If strict measures are not taken, pollutants will continue to grow at a fast rate due to the massive increase in energy use via the transport system. Bearing this in mind, the effects of emitted carbonaceous, tracer metal, gaseous and ultra-fine pollutants from a Euro IV diesel engine operated with biodiesel blend fuel were investigated in steady-state operating conditions. The baseline fuel was BC00 and the corresponding observations were recorded as a benchmark. With an increase in biodiesel, the experimental results showed an increase in aliphatic compounds, and a reduction in carbonaceous species and aromatic compounds, which can be explained due to the low amount of total PM2.5 mass present. CO and HC emissions were found to be within the Euro V emission limit, except for diesel and BC05 emissions. The emission of NOx and smoke significantly decreased across all biodiesel blends, which might be due to the occurrence of bonded oxygen with the absence of aromatics in the blend fuels which resulted in a reduction of soot nuclei formation, mainly in localized rich zones. However, some species such as zinc (Zn), calcium (Ca), sodium (Na), phosphorus (P) and vanadium (V) possibly remained in the diesel and could eventually be emitted as particles. Even though a proportion of the particles can be removed from the fuel via pre-heating, filtration or centrifuging, some may remain in the combustion air. It is often necessary to improve such unstable fuel by mixing it with a biodegradable fuel.

KEYWORDS: Diesel Engine; Trace Metals; Soot and Gaseous Particles; Organic Compounds & Biodiesel

<div style="text-align: right">*Original Article*</div>

1. INTRODUCTION

With rapid industrialization and urbanization, the demand for energy, infrastructure development and transportation has increased rapidly. Investigation reveals that transport activities are the major source of emitted greenhouse gas (GHG) emissions found in the environment [1,2]. Such gases have detrimental effects on human health and well-being. Among all the air pollutants, particulate matter (PM) such as $PM_{2.5}$ and PM_{10} is of particular concern. Due to their very small particle size, they can invade deep into human lungs and mix with the bloodstream [3]. As a result, chronic exposure to PM can cause many cardiovascular and pulmonary diseases [4]. Reduction of PM such as $PM_{2.5}$ and PM_{10} is crucial in any pollution abatement strategy. Investigation of PM and other pollutants from internal combustion engines provide information on pollutant concentration variability, its patterns and distribution of pollution in the region. This understanding also facilitates the identification of pollution sources.

Research in the transport sector on pollution abatement strategies has increased. The adverse effect of using distillate fuels in the transport sector has created significant interest in renewable energy, such as biofuels. The process of identifying suitable energy resources for the development of biofuel relies on cost, stability and

availability. Among the biofuels, biodiesel is said to be the most promising resource for use in industry, power generation and transportation with limited pollutant characteristics. Biodiesel has unique thermodynamic properties and its combustion in diesel engines produces less soot and particulate species, less ignition complications, high viscosity [5], and good inter-solubility [6]. Biodiesel blends in diesel engines need to be investigated regarding ultrafine nuclei, trace metal, carbonaceous species, aliphatic hydrocarbons, and polycyclic aromatic hydrocarbons (PAHs), because regulations regarding pollution are becoming very rigorous.

With the aim of mitigating GHGs and other pollutants, Verma et al. [7] examined the effect of soot particles from biodiesel blends. Results showed that the size of soot aggregates decreased with the increase of fuel-oxygen content, and the fractal dimensions increased significantly. Song et al. [8] investigated the oxidation behaviour of biodiesel soot and discovered that biodiesel soot showed rapid capsule-type oxidation rates with formation of graphene ribbon structures compared to Fischer-Tropsch (FT) diesel soot particles. Lapuerta et al. [9] found that the rate of soot particles was associated with oxidation reactivity. The results obtained showed that biodiesel soot primary particles were significantly smaller with a higher degree of graphitization than those of diesel soot. Engine load also had a significant influence on the properties of exhaust soot particles. Chen et al. [10], Hayashida et al. [11] and Man et al. [12] found that the effect of engine load is stronger than the effect of speed, and that smaller primary particles are formed due to faster soot oxidation under high environmental temperature [13]. In this regard, Lu et al. [14] found that when engine load is elevated, soot aggregates have a significantly higher number of primary particles. They attributed these results to the high temperature and pressure which causes the in-cylinder soot to be more highly oxidized, which promotes the oxidation rate of soot particles which is then higher than the specific active surface rate [15].

Recent investigations have focused on metallic ash content and organic aerosol species. Composition varies depending on fuel quality, engine type and age, and modification. Agarwal et al. [16] and Martin et al. [17] measured non-road emission factors of PM during B20 use and found that diesel had higher toxicity than the B20 blend due to PAH composition. Similarly, Lu et al. [18] evaluated the size distribution of organic carbon (OC), elemental carbon (EC) and PAHs emissions from the use of waste cooking oil biodiesel. They discovered that OC and EC decrease in biodiesel with a significant increase in mean diameter of PAHs compared to diesel fuel. The authors attributed the results to the highly effective reduction of combustion gleaned PAHs in nuclei mode.

Metals present in biodiesel and diesel PM might significantly contribute to the negative health impacts. Investigations have shown that metals, specifically transition metals such as Cu, Fe, Mn, Ni and V, are the major components of biodiesel and diesel PM [19–21]. Most of these metals vaporize during fuel combustion with nucleation forming before soot inception in the diffusion flame along with the formation of metal oxides [22].

Diesel engines are the source of heavy pollutants which are of particular concern. These are necessary to know about and to control because of their high emission values and health effects. If strict measures are not taken, pollutants will continue to grow at a fast rate due to massive increase in energy use via the transport system. For this reason, practical and policy implications associated with pollution directives need to be implemented in every country. In this study, the effect of emitted carbonaceous, trace metals, gaseous and ultra-fine pollutants from Euro IV diesel engines operated with diesel/biodiesel fuel were investigated at steady-state operating conditions.

2. METHODOLOGY

The research was carried out on a Cummins ISBe5.9 diesel engine which is 6-cylinder, turbocharged with common rail system. The research engine is capable of operating on Euro IV emission norms with a rated power of 230 hp @ 2500 rpm, with other specifications listed in Table 1. The engine was coupled to an in-house hydraulic dynamometer (electronically controlled). Figure 1 represents the schematic layout of the engine setup. Before experimental recording, lubricating oil, fuel leakage and coolant temperature were checked to ensure that they were the same as ambient temperature for safety purposes. At first, the research engine was allowed to operate with neat diesel fuel to obtain the baseline readings. For each test, 10 minutes were allocated for operation and 5 minutes were used for data recording. The test engine was started and run with a speed of 1800 rpm at no load condition and regular increment in load was performed till half-load (50%) mode. The main purpose of constant speed and engine load was to limit the number of factors that might influence the final results. The engine was embedded with LabView control system and an electronic control unit (ECU) to record and measure the values generated.

Table 1: Specification of Experimental Setup

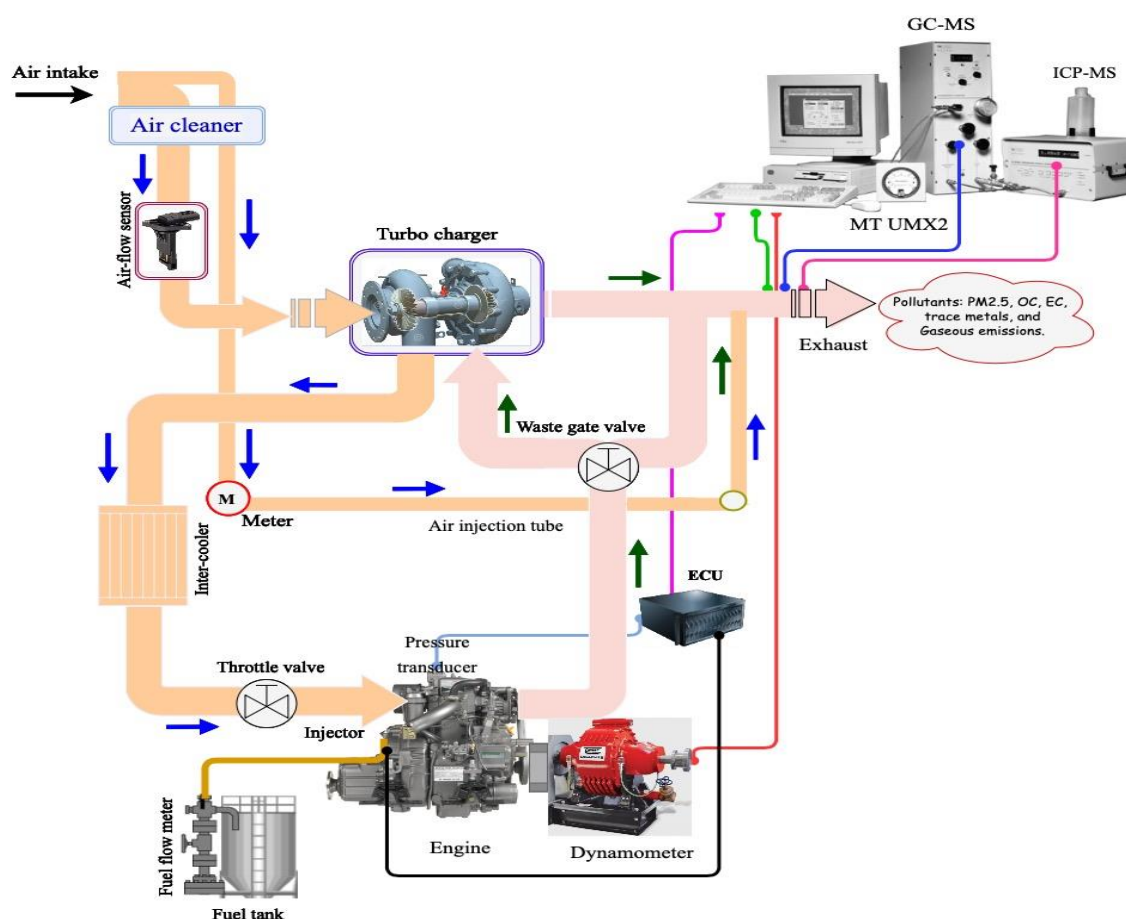| Engine Family: Cummins ISBe5.9	
Configuration	In-line, 6-cylinder, 4-stroke, diesel engine
Displacement	5.9 L
Bore x Stroke	102 mm x 120 mm
Fuel system	Common Rail System (CRS)
Rated power	220 hp @ 2500 rpm
Rated torque	800 Nm @ 1000 rpm to 1800 rpm
Aspiration	Turbocharged, Charge Air Cooled
Fuel type	BC00 (Diesel fuel), BC05, BC10 and BC15
Application	Bus
Emission norms	Euro IV

Figure 1: Schematic Layout of the Engine Setup.

The biodiesel (from waste cooking oil) was used as an operating blend with diesel fuel. The biodiesel was blended 5 %, 10 % and 15 % by volume and denoted as BC05, BC10 and BC15, respectively. The fuel properties are listed in Table 2. Compared with conventional diesel, the fuel blend had significant differences in properties. Even a small alteration in fuel properties is enough to create significant behavior differences in engine pollutants or performance.

Table 2: Fuel Properties

Properties	Unit	Diesel	Biodiesel BC100
Acid Number	mg of KOH/g	-	0.36
Density	kg/m^3	835	878.5
Kinematic Viscosity @40T	mm^2/sec	2.57	4.47
Oxidative Stability	hrs	4 to 6	8.4
Flash Point	°C	59	183.5
Cloud Point	°C	-5	0
Distillation @90 AET	°C	344	342.0
Cetane	-	56.5	54
Ash	mass %	0.002	0.005
Carbon Residue	mass %	0.19	< 0.002
Phos. Content	ppm	-	< 1.4
Group I-II Metals	ppm	-	< 1.3
Water Sediment	%vol	-	0.003
Free Glycerin	%vol	-	0.001
Total Glycerin	%vol	-	0.014

The effective way to evaluate the impact of blend fuel on pollutants is to allow the research engine to operate without any after-treatment system; this is to ensure that the pollutants do not depend on the after-treatment device. The AVL-444 exhaust gas analyzer was acquired to measure NOx, CO and HC emissions based on electrochemical and non-dispersive infrared (NDIR) principles. During experimental analyses, the total PM2.5 mass was determined by means of the net wet measurement process of a Teflo® filter (pollutant sample collector) using a Mettler Toledo UMX2 microbalance. The EC and OC emissions (PM mass) were analyzed using Tissuquartz filters as described in the NIOSH method [23]. Only some of the samples were collected on Pall Corporation Ann Arbor filters which were pre-conditioned for about 4 hours at 550 °C then stored in a temperature of less than 5 °C as per [23]. The remaining sample of Tissuquartz filters in EC/OC emission was extracted with methylene chloride and analyzed via EPA TO-13A_GC-MS [24]; this was to determine the rate of organic compounds such as PAHs, C10 to C30 hydrocarbons and Benzo(ghi)perylene. Furthermore, the metal nanoparticles were characterized via inductively coupled plasma-mass spectrometry (ICP-MS) from the size-segregated NanoMOUDI substrates. The properties of the trace metals V, Cr, Fe, Ni, Cu, Na, Al, Ba, K, Zn, Ca and etc., along with their relative efficiencies, were investigated due to their high toxicities as discussed in [25, 26].

3. RESULTS AND DISCUSSIONS

3.1. Carbonaceous Species and Organic Compounds in PM$_{2.5}$ Mass Emissions

Figure 2(a) shows the significant variability in PM$_{2.5}$ mass emission factors at various blend ratios. From the Euro (V) steady-state testing procedure, most of the total carbonaceous species (EC+OC) were not in accordance with PM emission standard limits, except for BC15 fuel with 0.018 g/kW-h. This is explained by the fact that during high temperature and pressure, EC and OC formed in the fuel-rich zone decrease as more droplets of fuel are injected into the cylinder. The BC00 and BC05 emissions were deeply affected by the other parameters, leading to the variable correlation between fuel and operation mode. It was found that EC levels were slightly higher compared to OC levels within all the tests, which can be explained due to the low amount of total PM$_{2.5}$ mass present. This suggests that the thermal optical method may not gain essential sources for PM$_{2.5}$ mass from oxidized species like organic acids and esters [27].

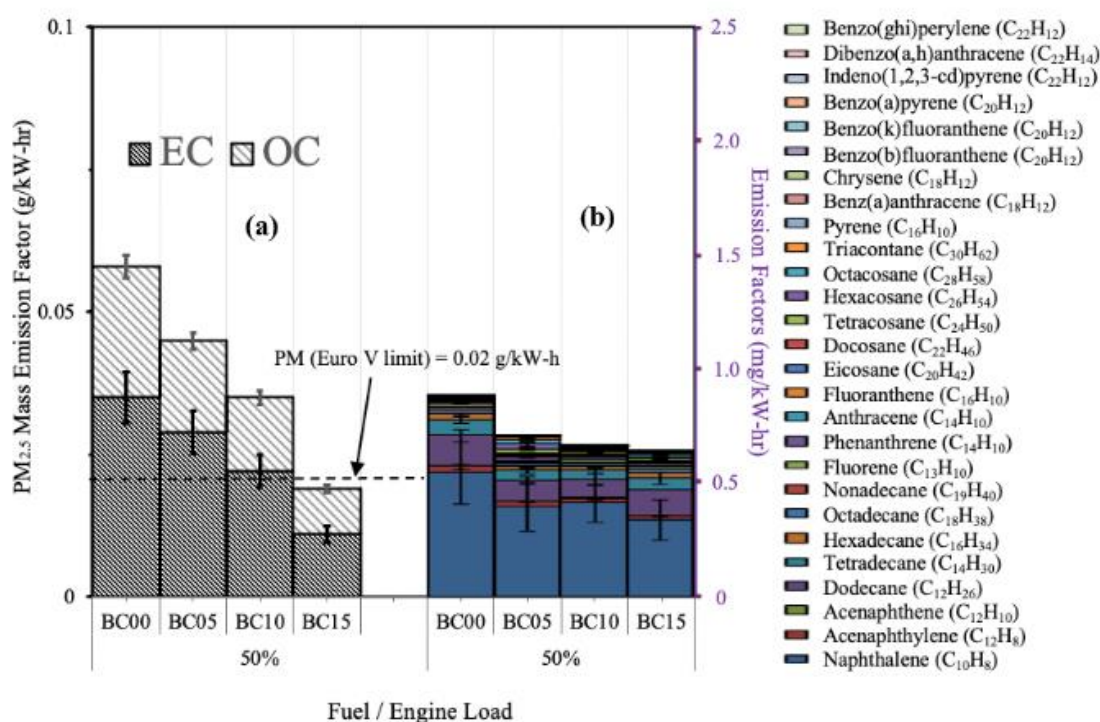**Figure 2: Effect of Fuel Variability on (a) Speciated PM2.5 Mass Emission Factors (b) Composition of Particulate Organic Matter at Steady-State Mode.**

Figure 2(b) displays the variability of emission factors with carcinogenic potentiality which might require regulation. The carcinogenic risks associated with alkane and PAHs are of particular concern due to their very small particle size; they can penetrate deep in the human lungs and can also mix into the bloodstream [3]. From the PAHs results, it was found that naphthalene was dominant at low and medium temperature levels of all blend fuels. Even with no after-treatment, the experimental results showed a reduction in aromatic compounds and a slight increase in aliphatic compounds. The high n-alkane species such as dodecane, hexadecane, hexacosane and tetradecane were observed for the baseline test followed by BC05 fuel. These originated from unburned oil as well as diesel fuel. The combustion of BC15 showed reduced PM related PAHs emissions compared to BC00 fuel, with low emission rates of pyrene, chrysene, anthracene and phenanthrene compared to results found by [17,28]. The emission factor results showed that BC15 was less toxic compared to BC12, BC05 and BC00. This finding is consistent with emissions from cottonseed oil biodiesel [29], and soybean oil biodiesel [30].

3.2. Gaseous emissions

3.2.1. CO and HC Emissions

Figure 3 represents the variation of CO and HC emissions in an indicated range with various blend fuels. The emission of CO and HC limits for Euro V at steady-state testing procedures were 1.5 g/kW-h and 0.46 g/kW-h, respectively. The results indicate that CO and HC emissions were within the Euro V emission limits, except for BC00 and BC05 emissions. CO is one of the combustion components and its complete combustion leads to CO_2. The factors such as unavailability of oxygen and incomplete combustion lead to CO emission. In this context (as seen from Figure 3), the competition between CO and HC for O_2 leads to more CO oxidation than the increase in HC conversion efficiency so the conversion of CO is not complete.

The Effect of Low-Carbon Fuel on Trace Metals, Organic Compounds, Gaseous
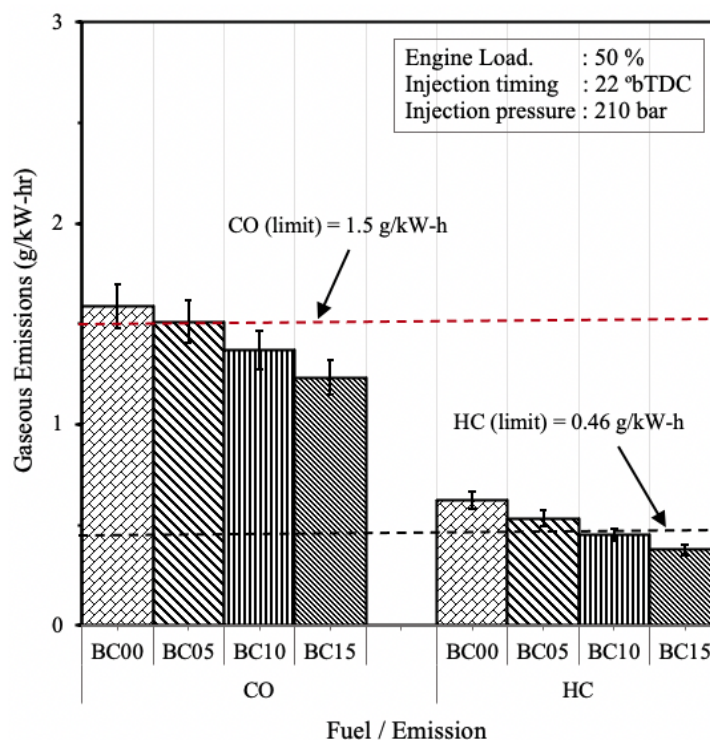*and Particulate Species from a Euro Iv Diesel Engine at Steady-State Mode*

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**Figure 3: Variation of CO and HC Emissions in an Indicated
Range with Various Blend Fuels at Steady-State Mode.**

With the increase in biodiesel, CO and HC emissions were fully combusted, and incompletely burnt fuels such as in BC00 and BC05 comprised a large mass fraction of the pollutants at low-combustion temperatures. Biodiesel aids in the conversion of HC due to the improved oxidation characteristics and presence of high in-cylinder temperatures causing complete fuel burn which results in less HC emission levels. Previous work has reported that poor fuel atomization and low temperatures lead to flame quenching especially during various phases [31], which in-turn decreases combustion efficiency and elevates CO and HC emissions in low blend fuels [32].

3.2.2. NOx and Smoke Emissions

As shown in figure 4, the NOx emission of BC10 and BC15 were within the Euro V standard limits at steady-state operating conditions. Results imply that an increase in fuel oxidation number had a positive effect on NOx emissions. This was also observed by [33], that the emission of NOx decreased somewhat at 50 % engine load. The attribution was due to the reduction in premixed combustion which leads to an advance in combustion timing during fuel pre-injection. Similarly, the blend fuel becomes more saturated as a result of variable cetane number, yield the adiabatic flame temperature decreases. Factors affecting the NOx emission formations were combustion temperature, residue time, fuel oxidation, ignition delay and monolith temperature.
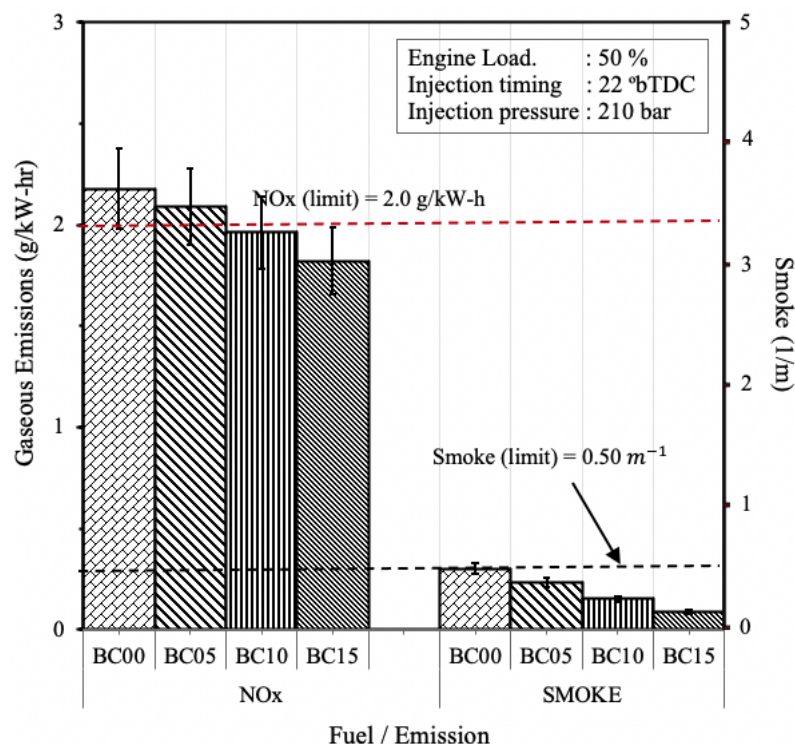
Figure 4: Variation of HC and Smoke Emissions with Various Blend Fuels in Steady-State Mode.

Smoke is considered as a soot emission indicator, and is caused due to unburnt fuel in the combustion of carbon particles and hydrocarbons [34, 35]. It was observed that low smoke emission values were obtained from all the biodiesel blends except BC00. This reduction of smoke was lower than the Euro V standard limits according to the steady-state testing procedure. This was attributed to the occurrence of bonded oxygen with the absence of aromatics in the blend fuels which results in reduction of soot nuclei formation mainly in localized rich zones.

3.3. Emission of Trace Metals

The emission properties of trace metals such as V, Cr, Fe, Ni, Cu, Na, P, S, Al, Ba, K, Zn and Ca were investigated because of their high toxicities. As can be seen in Table 3, the dominant trace elements were Cu, V, Zn, and Fe. These species are redox-active transition metals which can cause oxidative damage to cellular membrane lipids, causing cardiovascular and pulmonary diseases [36,37]. In this study, V constituted 33.06 μg/kW-h of the diesel emissions, Cu 61.15 μg/kW-h, Zn 103.91 μg/kW-h and Fe 59.98 μg/kW-h, all of which are more harmful than any of the lighter metals. When a high content of V is present in the fuel then the engine should operate with exhaust temperatures of less than 723 K to eliminate the risk of hot corrosion. The majority of soot species emitted during the combustion process are usually associated with the content of metals in the fuel and this varies depending on the source of the fuel. The relative presence of Na and Ni emission species were slightly higher in the biodiesel blends than the BC00 fuel. These species possibly remained in the biofuel and eventually emitted as particles. Na can be removed from fuel through centrifuging even though some particles may remain in the combustion air. The Ca, P and Zn species in the blend fuel particles were likely to have originated mainly from the engine lubricant [38].

Table 3: Emission of Metal Species in Particulate Matter at Steady-State Mode

Metals	BC00	BC05	BC10	BC15
	Engine load: 50 %, Injection Timing: 22 º bTDC (µg/kW-h)			
Al	50.42	48.39	45.55	43.28
Ba	9.87	8.01	7.27	6.41
Ca	90.58	92.16	96.14	99.16
Cr	7.44	7.33	7.12	7.01
Cu	61.15	60.07	58.45	56.19
Fe	59.98	54.28	47.42	41.88
K	20.41	18.53	12.44	9.02
Na	73.32	78.23	80.64	82.81
Ni	5.59	7.12	9.40	13.77
P	78.11	83.64	88.57	90.28
S	50.87	51.01	51.49	51.76
V	33.06	22.68	17.06	10.11
Zn	103.91	100.11	95.43	90.94

The sulfur (S) content found in the particles was linked to the portion of unburned fuel present on the soot surface. Apart from the risk of pollution from fuel containing a high sulfur content, there are combustion problems as well that one needs to be aware. During combustion of such fuel, the S burns to form different oxides of sulfur, which associate with water vapor produced by combustion to cause acidic vapors. Also, when the surface temperature in the combustion chamber or exhaust system falls below the condensing temperature (the dew point) of these vapors, then liquid acid will form on the surfaces. This can lead to cold corrosion of the surfaces, but can be prevented using cylinder oils with a suitable alkalinity or base number to maintain surface temperatures above the dew point whenever possible.

4. CONCLUSIONS

The effect of emitted carbonaceous, trace metals, gaseous and ultra-fine pollutants from a Euro IV diesel engine operated with biodiesel blend fuel were investigated at steady-state conditions. The baseline fuel was BC00 and the corresponding observations were recorded as a benchmark. Some of the particulate, gaseous and trace metal species from the biofuels were within the Euro V emission standard limits at steady-state operating conditions. The results obtained are summarized as follows:

- The experimental results showed a reduction in aromatic compounds with a slight increase in aliphatic compounds. Thus, it was found that EC levels were slightly higher compared to OC levels within all tests, which can be explained as being due to the low amount of total PM2.5 mass present.

- CO and HC emissions were found to be within the Euro V emission limit, except for the BC00 and BC05 emissions.

- The emission of NOx and smoke decreased somewhat across all biodiesel blends. This was attributed to the occurrence of bonded oxygen with the absence of aromatics in the blend fuels which results in the reduction of soot nuclei formation mainly in localized rich zones.

- The trace elements of the fuel emissions were dominated by Zn, Ca, P, Cu, V. These species possibly remained in the biodiesel and eventually emitted as particles.

- Standard limits are intended to reduce the atmospheric pollution from engines and vehicles which can cause health and environmental problems. Even though a proportion of the particles can be removed from the fuel via pre-heating, filtration or centrifuging, a portion may still remain in the combustion air. Therefore, to make use of unstable fuel, it is often necessary to improve it by mixing it with a biodegradable fuel.

CONFLICT OF INTEREST

None

ACKNOWLEDGEMENT

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